

POLYIMIDE MATRIX RESINS FOR UP TO 700°F SERVICE

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1.0 INTRODUCTION

Linear aromatic/heterocyclic condensation polyimides were the first candidates of this generic type of polymer to find acceptance as an item of commerce. Different types of the linear condensation polyimides have been qualified for many aerospace applications including matrices for high performance seals, bushings, bearings and radomes as well as wire coatings and other applications. Upper use temperatures in air normally employed for the first generation linear condensation polyimides were 316°C (600°F) and below.

A series of linear condensation polyimides have appeared on the market beginning in the 1960's for high performance resin applications. The polymer systems that have endured as viable commercial systems include such resins as Skybond polyimides from Monsanto (Reference 1) and the Vespel and Kapton polyimide products available from Du Pont (References 2 and 3).

In the mid-1960's, when requirements began to emerge for high performance, large airframe structures fabricated from polyimides, key deficiencies inherent with linear condensation polyimides began to manifest themselves. Upon attempts to compression mold thick reinforced laminates and/or autoclave fabricate composite structures, the continual evolution of residual solvent and aqueous condensation volatiles consistently led to high void content products which were unsuitable for most structural applications. Also, the normally existing high molecular weight state of the linear condensation polyimides required processing parameters, particularly high pressures, which continue to be beyond the capability of state-of-the-art autoclave fabrication hardware. These deficiencies prompted the trade to investigate alternative polyimide approaches to the linear condensation materials.

The quest for alternative high performance resins to linear condensation polyimides began in the mid-1960's. The major thrust in this work

emphasized research on technology which minimized evolution of volatiles during fabrication and cure as well as alteration of resin molecular weight to promote facile autoclavability at pressures of 1.3 MPa (200 psi) or less. The two most successful alternative polyimide approaches which give resins suitable for longer-term service at temperatures up to 316°C (600°F) are the norbornene and acetylene terminated polymers.

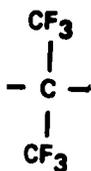
In 1966, TRW discovered that low molecular weight (e.g., 1000 g/mol to 2000 g/mol) polyimide prepolymers terminated by nadic anhydride processed in a significantly easier fashion than the linear condensation polyimides. Addition cure through the elements formed from the nadic moiety at 316°C gave essentially void free composite structures. This work led to introduction of a commercial product designated P13N (Reference 4). Significant ingredient formulary improvements at NASA Lewis Research and NASA Langley Research Centers have led to new polyimide products designated PMR-15 and LARC-160 resins, respectively (References 5 and 6, respectively). Each of the improved products are finding wide trade acceptance as autoclavable, high performance polyimides and have essentially replaced P13N.

While TRW was investigating the technology that led to P13N, research at Hughs Aircraft Company discovered that polyimide prepolymers, terminated in aromatic acetylene derivatives, gave cured polymers possessing processability, low void content and high temperature use characteristics very similar to P13N. These acetylene terminated resins have been designated HR-600-type polyimides (Reference 7). Development work on improved polyimide modifications is continuing at Hughes Aircraft Company (Reference 8).

During the late-1960's, the addition-type polyimides discussed above fulfilled most requirements for high performance resins. This was primarily as a result that needs did not exist for resins that required stability at 316°C (600°F) to 371°C (700°F) in air for hundreds to thousands of hour service lifes. However, beginning in the mid-1970's, advanced jet engine development (e.g., Pratt and Whitney's F-100 and GE's F-101) sought matrix resins suitable for use at >> 316°F in air atmospheres ranging up to 0.4 MPa (60 psia). These engine requirements prompted additional polyimide

development which has led to identification of second generation, very thermo-oxidatively stable linear condensation polyimides which possess a new type of backbone linkage in the aromatic polyimide backbone.

The initial second generation linear condensation polyimide to be developed were resins containing a perfluoroisopropylidene linkage shown below in either the two ring dianhydride and/or diamine constituent of the



polymers. These polyimides were discovered by Du Pont and introduced to the trade as the NR-150B series of resin products (Reference 9). Although these high performance linear polymers demonstrated significant promise to meet several jet engine composite applications, general sale of the materials to the trade has been recently terminated.

Because of the unavailability of polyimide matrix resins for use at temperatures up to 371°C in air as dictated by the removal of NR-150B resins from the marketplace, TRW initiated development studies in 1980 to assess whether another second generation family of linear resins may be suitable for service at temperatures > 316°C. The new TRW polyimide resins, designated partially fluorinated polyimides, have given data which suggest they do indeed possess thermo-mechanical characteristics making them suitable for service in the temperature range of 316°C to 371°C in air. Ongoing development of the partially fluorinated polyimides as high performance composites matrix resins constitute the topic of this paper. Evaluation studies completed to date are presented and discussed in Section 2.

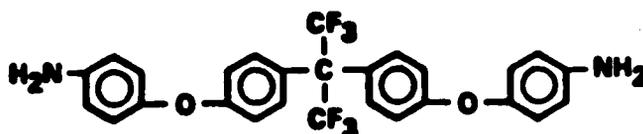
2.0 TECHNICAL DISCUSSION

TRW is in the process of data accumulation that strongly indicates that incorporation of the perfluoroisopropylidene linkage in molecular structures other than those employed in Du Pont's NR-150B polyimides likewise yield polymers demonstrating extremely high thermo-oxidative stability. Polyimide synthetic and characterization studies conducted to

date on new polymers incorporating the perfluoroisopropylidene linkage are presented and discussed below.

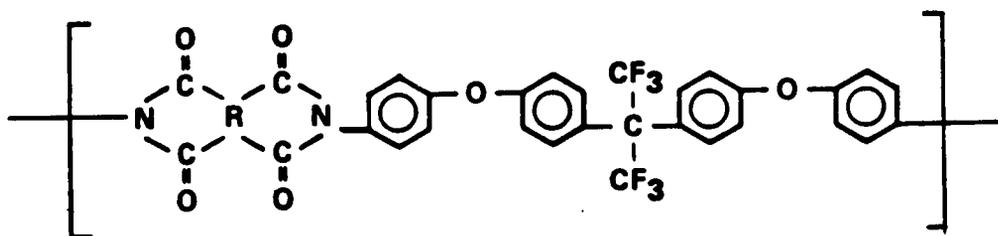
2.1 PARTIALLY FLUORINATED POLYIMIDE CHEMISTRY

TRW has discovered that use of a partially fluorinated aromatic diamine 2,2-bis[4-aminophenoxy]phenyl]hexafluoropropane (4-BDAF, see structure below) yield linear condensation polyimides possessing con-



4-BDAF

siderable promise for long term service in highly oxidative environments at temperatures up to 371°C. The 4-BDAF monomer and polyimides therefrom were discovered in 1975 on NASA Lewis Research Center Contract NAS3-17824 (Reference 10). The diamine monomer and polyimide resins are described and claimed in U.S. Patent Numbers 4,203,922 and 4,111,906 (Reference 11 and 12), respectively. A general structure for polyimides prepared from 4-BDAF diamine is presented below.



WHERE R = AROMATIC RING STRUCTURE

The promise shown in 1980 and 1981 for the 4-BDAF diamine as a key starting ingredient for high performance polyimides prompted Morton Chemical Company to express interest to become a qualified source of supply for the material. After two years of synthesis process and purity

assessment, Morton has recently obtained an exclusive license from TRW to commercially produce and sell the diamine under the art taught in U.S. Patent Number 4,203,922. Limited availability of the product to the trade is anticipated to occur in 1983.

2.2 INVESTIGATION OF PARTIALLY FLUORINATED POLYIMIDES AS A MATRIX FOR 357°C (675°F) SERVICE

Although, as previously stated, the linear condensation polyimides from 4-BDAF diamine were discovered in 1975, directed research and development activities on the diamine and polyimides therefrom was not undertaken at that time due to lack of clearly identifiable markets for products. In 1980, in response to urging by the jet engine primes and government agencies, TRW initiated studies to determine whether the partially fluorinated polyimides produced from 4-BDAF diamine could serve to replace currently available condensation polyimides as well as serve as a potential substitute for the very high performance linear resins offered by Du Pont as the NR-150B family of polyimides.

The 1980 studies on the TRW partially fluorinated polyimides were structured to assess basic thermo-oxidative stability, glass transition temperature and processability characteristics related to potential use as a jet engine compressor stage stator vane bushing at a service life temperature of 357°C (675°F). This effort was jointly sponsored by the GE Aircraft Engine Group, Evendale, Ohio and the Bearings and Applied Technology Divisions of TRW. In this study, a number of significant discoveries were made as summarized below.

Two candidate polyimide polymers were prepared from pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic acid dianhydride (BTDA) employing TRW's 4-BDAF as the diamine ingredient at the Redondo Beach, California facility. Solutions of the amide-acid precursor were supplied to the TRW Bearings Division, Jamestown, New York for processing studies. The amide-acid solutions were converted into polyimide molding compounds employing Celanese's GY-70 high modulus chopped graphite at a 50% by weight level as the reinforcement. The two candidate materials were compression molded into resin discs of dimensions approximately one-inch in diameter by one-inch thick. Prototype jet engine compressor stator vane bushings

were machined from the discs to 0.001-inch tolerances. A photograph of the prototype bushings is provided as Figure 1.

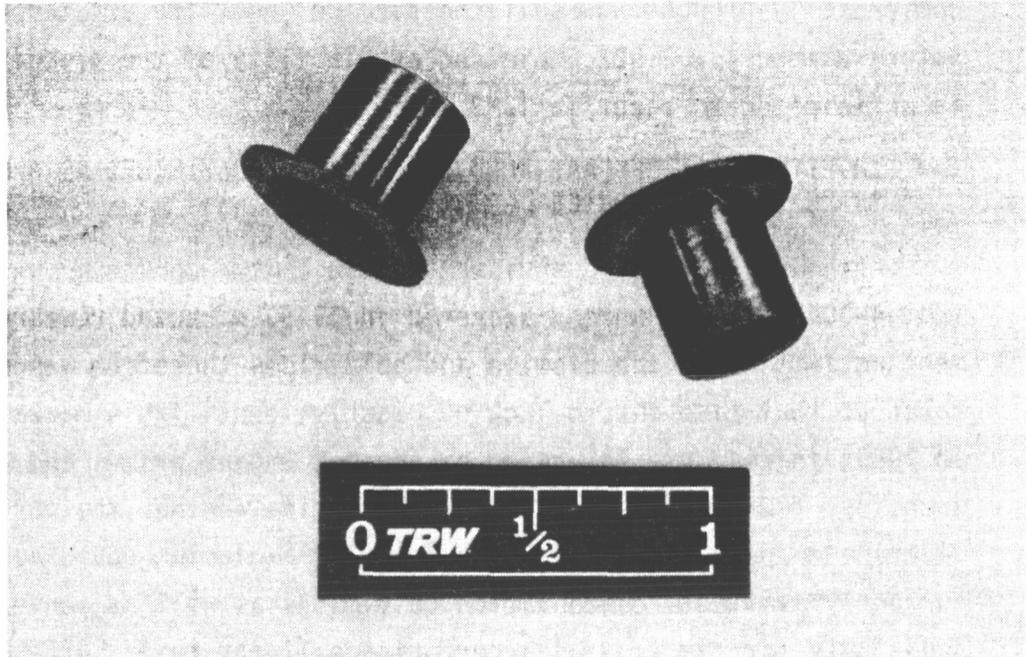


Figure 1. Prototype Jet Engine Stator Vane Bushings

Resin disc samples of each of the two candidate polyimides were provided to GE for oxidative and thermo-mechanical testing. The two polyimide candidates were subjected to the GE oxidative screening test which consists of a one hundred hour exposure at 357°C under a four atmosphere flow of compressed air. The results from this test and related thermal measurements are presented in Table 1. For the purposes of GE product interests, the 4-BDAF/BTDA formulation was definitely unsuitable for further consideration due to its weight loss at 675°F and the surprisingly low glass transition temperature of ~ 310°C. Conversely, although the weight loss was relatively high for the 4-BDAF/PMDA formulation, the highly desirable T_g of this candidate of ~ 390°C was held to be very promising and the material was deemed worthy of further study.

Subsequent joint GE/TRW studies on polymer development have yielded neat molded 4-BDAF/PMDA specimens which give a weight loss of only 8% at 357°C. A key factor in this significant product improvement is thought to be the current high quality of the 4-BDAF diamine produced by Morton Chemical on up to 50-lb/run batches. The initial work employed

diamine synthesized at TRW on a much smaller scale. The stator vane bushing development effort is continuing employing diamine produced by Morton Chemical.

TABLE 1
PARTIALLY FLUORINATED POLYIMIDE THERMAL ANALYSIS PROPERTIES

Property Measurement	Experimental Results	
	4-BDAF/PMDA	4-BDAF/BTDA
Glass Transition temperature (T _g) ^{a)}	390°C (734°F)	310°C (590°F)
Onset temperature of oxidatives degradation ^{b)}	495°C (923°F)	490°C (914°F)
Isothermal aging in air (% weight loss) ^{c)}	20	34

- a) Determined on a Du Pont Model 990 thermalmechanical analysis attachment operating in a penetration mode.
 b) Determined on a Du Pont Model 990 thermalgravimetric analysis attachment employing a 3°C/minute heat-up rate and 100cc/minute air flow.
 c) Determined on composite discs containing 50% by weight GY-70 chopped fiber reinforcement; aging conditions consisted of a 675°F temperature for 100 hours employing a four atmosphere compressed air flow.

The initial promise of the GE/TRW study on the partially fluorinated polyimide prompted TRW to initiate investigation of other resin matrix applications. Initial lubricity and wear test results are the subject of a NASA Lewis Research Center technical publication (Reference 13). Additional tribological property evaluations are being conducted by TRW on NASA Lewis Research Center Contract NAS3-23054 (Reference 14). Assessment of the partially fluorinated polyimides as a matrix for high performance hydraulic seal back-up rings is planned for study at TRW on USAF Contracts F33615-81-C-5092 and F33615-82-C-5021 (Reference 15 and 16, respectively). A summary of properties other than thermal measurements determined in these and related property assessment studies is provided in Table 2.

TABLE 2
 REPRESENTATIVE PARTIALLY FLUORINATED POLYIMIDE PROPERTIES

Property Measurement	Results
Specific Gravity	~ 1.4 ^{a)}
Hydrolytic Stability	No degradation observed in two hours water boil ^{b)}
Solvent Resistance	No degradation noted in methyl-ethyl ketone and jet reference fuel soak ^{b)}
Filler Compatibility	Amenable to fibrous and powder filling to at least 50% by weight ^{a)}
Filler Wetting	Excellent (photomicroscopy) ^{a)}
Machinability	Excellent (0.001 to 0.002-inch tolerance) ^{a)}

a) Determined on compression molded discs.

b) Determined on films of nominal 0.005-inch thickness.

2.3 INVESTIGATION OF PARTIALLY FLUORINATED POLYIMIDES AS A MATRIX FOR 371°C (700°F) SERVICE

In 1982, TRW initiated studies on NASA Contract NAS3-23274 to investigate monomer ingredient modifications intended to upgrade the baseline 4-BDAF/PMDA polyimide (see Section 2.2) to render the partially fluorinated polyimides suitable for $\geq 371^\circ\text{C}$ service in highly oxidative environments. The requirement for 371°C matrix resins has been stated by jet engine primes for future advanced jet engine systems.

A total of five new linear condensation polyimides were prepared and characterized in Contract NAS3-23274. Specifically, each of the following polyimides were synthesized (please see Table 3 for monomer structures):

- 2-C1-4-BDAF/PMDA,
- 2-C1-4-BDAF/6-FDA,
- 4-BPDA/PMDA,
- 4-BPDA/6-FDA and
- 4-BDAF/6-FDA.

TABLE 3
 MONOMERS SELECTED FOR STUDY ON CONTRACT NAS3-23274

Monomer Name/Abbreviation	Monomer Structure
Pyromellitic Dianhydride (PMDA)	
2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6-FDA)	
2,2-Bis[4-(3-Halo-4-aminophenoxy)phenyl]hexafluoropropane a (3-H-4-BDAF)	

TABLE 3 (CONTINUED)
 MONOMERS SELECTED FOR STUDY ON CONTRACT NAS3-23274

Monomer Name/Abbreviation	Monomer Structure
2,2-Bis[4-(2-halo-4-aminophenoxy)phenyl]-hexafluoropropane a) (2-H-4-BDAF)	
4,4'-Bis(4-aminophenoxy)biphenyl (4-BPDA)	
2,2-Bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (4-BDAF)	

a) Chlorine has been selected as the halogen atom to be initially introduced.

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The synthesis, characterization, processing and evaluation of these new polyimides is described below.

The resins were synthesized as their polyimide-precursors in dimethyl acetamide employing a resin varnish solids loading of twenty-five percent by weight. The polyimides were prepared by solvent removal and imidization in the temperature range of 100°C to 200°C. The resins were then post-cured at 371°C. Each polyimide demonstrated an initial weight loss by thermalgravimetric analysis (TGA) in air at a minimum of 490°C. The TGA results were deemed encouraging towards a goal isothermal stability of 371°C. A representative thermogram is presented in Figure 2.

The five new polyimides were isothermally aged as powders (nominal twenty-five mesh particles) for two hundred and forty hours at 371°C employing an ambient atmospheric air flow of ten cubic centimeters per minute. Both 4-BDAF/PMDA powder and a neat resin molded disc were included in the aging study to serve as control specimens.

The results of this 371°C aging study are plotted in Figure 3. The 371°C isothermal stability of 2-Cl-4-BDAF/PMDA, 2-Cl-4-BDAF/6-FDA and

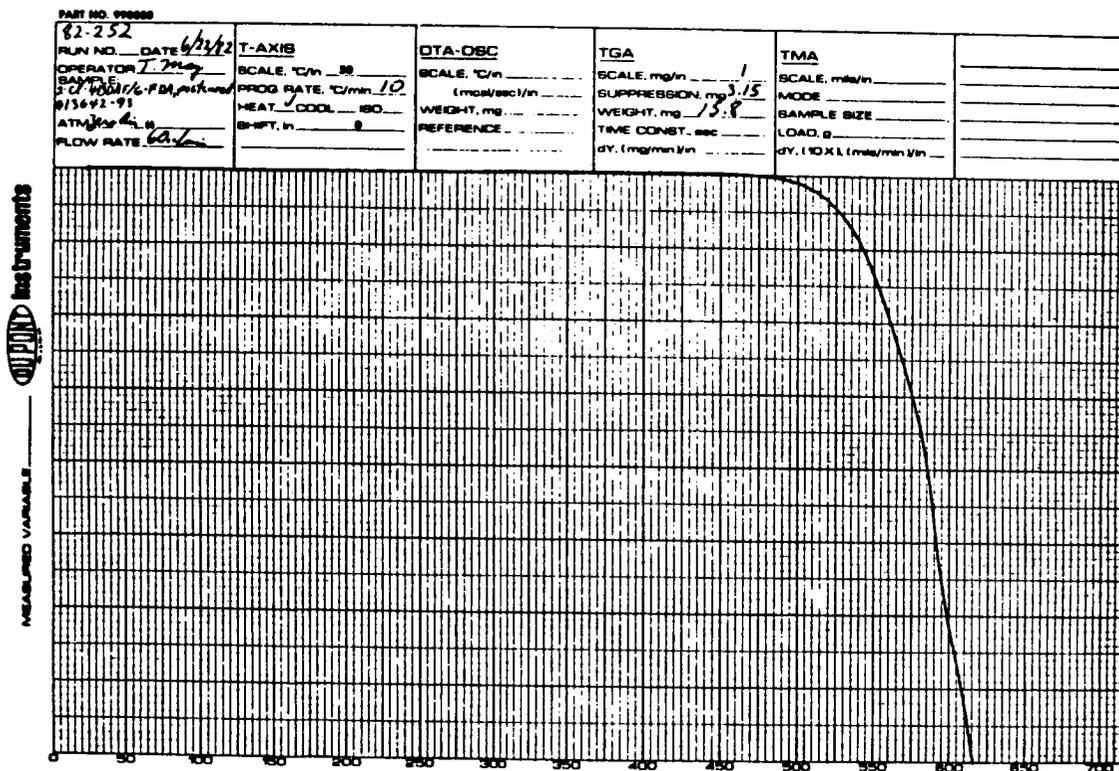


Figure 2. Thermogram of 2-CL-4-BDAF/6-FDA.

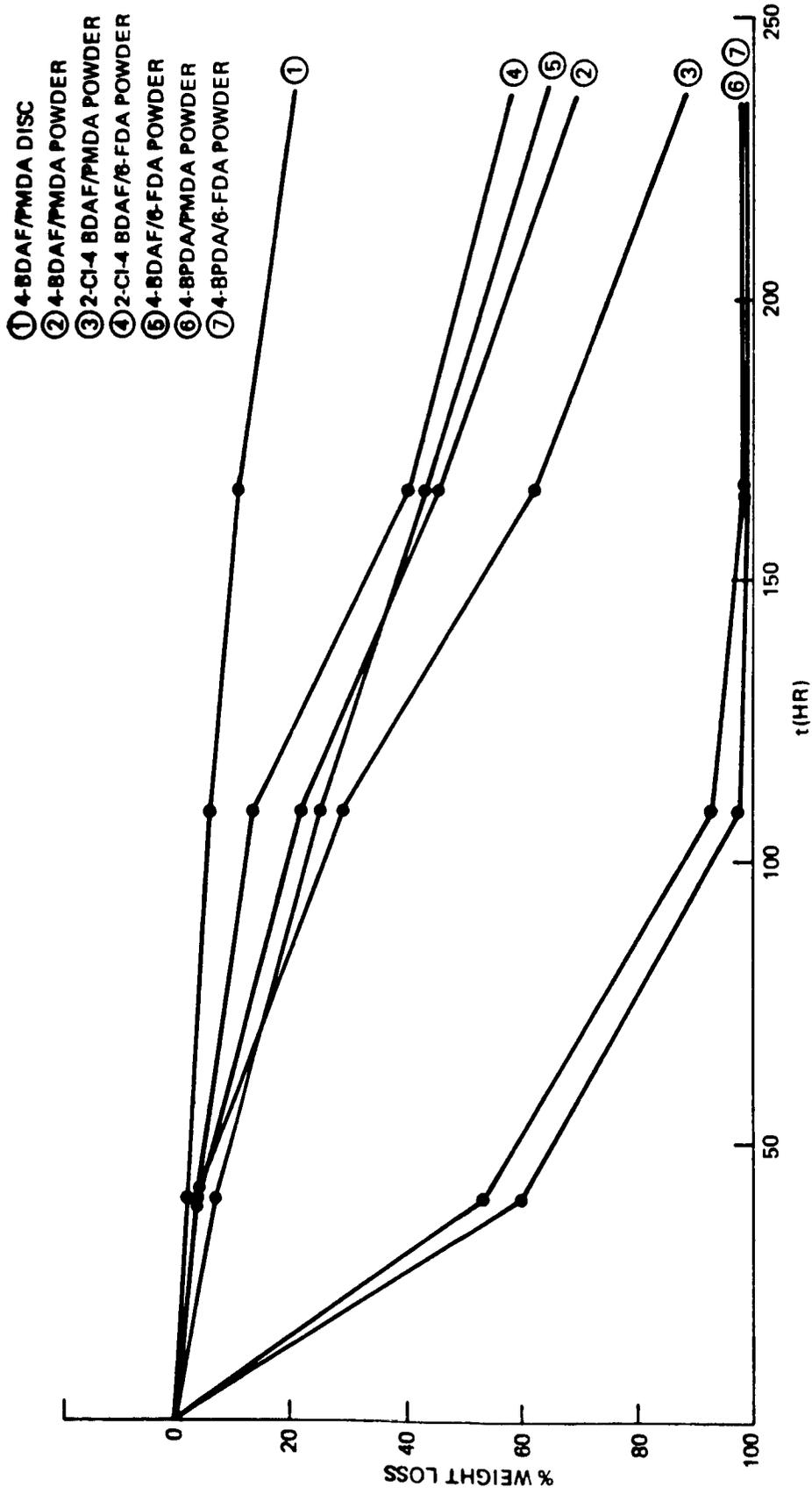


Figure 3. Isothermal Aging Results at 371°C for Partially Fluorinated Polyimide Candidates.

4-BDAF/6-FDA were judged to be promising. Comparison of the weight loss of these polyimides and the 4-BDAF/PMDA controls as powders of up to approximately thirty percent with the 4-BDAF/PMDA disc weight loss of six percent after one hundred hours (the minimum goal for jet engine performance) gave promise that each new resin had the potential as an excellent candidate for 371°C service. Conversely, the 4-BPDA/PMDA and 4-BPDA/6-FDA resins demonstrated surprisingly poor thermo-oxidative stability at 371°C and were eliminated from further consideration as high performance matrix resin candidates.

Neat resin fabrication studies were conducted on the promising new polyimide candidates and the 4-BDAF/PMDA control. It was determined that compression molding temperatures and pressures up to 450°C (850°F) and 408 MPa (6000 psi), respectively, are required for the polyimides. These processing parameters yielded neat resin discs of up to 6.35-cm (2.5-inch) diameter discs which were essentially void-free and possessed specific gravities in the desired range of 1.40 to 1.45. A representative compression molding cycle is presented in Table 4.

Completion of the processing studies, thermalmechanical analysis (TMA) determination of glass transition temperatures and isothermal aging of molded discs at 371°C and compressed air pressures up to 0.4 MPa (60 psia) for durations of up to two hundred and forty hours is in progress. The results of these key tests will be presented.

3.0 CONCLUSIONS

Based upon the test results completed to date, TRW offers the following conclusions concerning partially fluorinated polyimides as matrix resins for up to 371°C (700°F) service in air:

- The polymers can be easily prepared by conventional linear condensation methodology
- Neat resin glass transition temperatures of a minimum of 390°C are achievable
- Several polymer candidates have demonstrated promising thermo-oxidative stability at 371°C for a minimum of one hundred hours in flowing air at ambient atmospheric pressure

TABLE 4
 SUMMARY OF A REPRESENTATIVE MOLDING CYCLE EMPLOYED
 TO FABRICATE NEAT RESIN FORMULATION 4-BDAF/PMDA

Time at Temperature (minutes)	Bumping Cycles Performed (0 to 3408 MPa/6000 psi)	Mold Temperature (°C/°F) ^a
0 to 30	8	284°C/544°C to 334°C/633°C
31 to 60	9	334°C/633°F to 385°C/725°F
61 to 100	8	385°C/725°F to 416°C/780°F
101 to 120	0 ^b)	416°C/780°F to 452°C/846°F
121 to 150	0 ^b)	452°C/846°F to 456°C/853°F

^a Average of three thermocouple measurements.

^b Pressure was applied constantly at 408 MPa.

- Several polymer candidates are amenable to compression molding into defect-free neat resin parts

It is believed that synthesis and fabrication process optimization, coupled with fibrous reinforcement, will yield partially fluorinated polyimide matrices suitable for a minimum of one hundred hour service at 371°C under 0.4 MPa compressed air pressures.

4.0 ACKNOWLEDGEMENT

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